

Molecular structure effects in photodegradation of phenol and its chlorinated derivatives with phthalocyanines

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Abstract

In this work we report on possible utilisation of sulphonated phthalocyanines as efficient oxidation catalysts for the removal of various traces of chlorinated compounds from an aquatic environment. Photocatalytic oxidations were carried out with visible and ultraviolet light in agreement with location of their distinctive absorption bands in both these regions. The reaction rate of decomposition of the substrate was measured as a function of pH. Special attention was paid to describe aggregation of the photocatalyst resulting in significant decreasing of the photooxidation activity. Suppression of this undesirable phenomenon by addition of some alcohol to the reaction mixture was studied in detail. Photocatalytic efficiency was verified according to calculated quantum yields.

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1. Introduction

Phenol and its derivatives are industrially important chemicals and thus their presence in the environment is relatively very common [1,2]. Due to their high toxicity [3–5], they represent a group of dangerous chemicals even at low concentrations. Chlorinated phenols may also be produced, not intentionally, whenever chlorination treatment of water is performed. In such cases, trace levels of phenol are transformed into chlorinated derivatives representing a specific risk especially for prolonged exposures [6]. There have been a number of methods describing the effective treatment of waste water contaminated with phenolic compounds [2,7,8]. Among many available technologies, photooxidation processes play an important role. However, they are mostly limited to systems illuminated with the highly energetic UV photon flux [9,10]. This approach is

typically represented by utilisation of TiO₂ semiconducting particles providing positively charged holes as effective oxidation species upon UV illumination [11,12]. The necessity of UV is a substantial disadvantage of this method. Visible light sensitised TiO₂-based photocatalysts have also been repeatedly reported, e.g. [13–16]. Phthalocyanines (PHCs), especially those containing metal ions with fully occupied d-orbitals, could be referred to as attractive alternatives for the visible light induced photocatalytic decomposition of phenolic compounds in homogeneous phase. Photoactivity of phthalocyanines arises from their ability to produce highly active singlet oxygen species ¹O₂ upon photon flux absorption in either UV or visible parts of the spectrum. This singlet oxygen is formed during the extinction mechanism of the excited triplet state following its collision with molecular O₂. Details on this mechanism are given elsewhere [17–21]. It must be noted that besides this property, phthalocyanines reveal very good photostability [22] and negligible toxicity. It is believed that, even at low concentrations, they might be seriously considered as practically available photooxidation catalysts for the treatment of water contaminated with many toxic chemicals.

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In this paper we report on the activities of a series of phthalocyanines (AlPHC, SiPHC, ZnPHC and metal-free PHC) in the photooxidative decomposition of phenol and its chlorinated derivatives upon distinctive illumination in the visible and UV part of spectrum. This article is a continuation of our recently published paper [23] briefly describing the preparation of PHCs and optimisation of the photooxidation experimental setup. In this work phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol were used with the primary intention to assess the effect of the chlorination extent and the substituent location on the course of photooxidation. To the best of our knowledge, data arising from similar experiments have not been reported yet.

2. Experimental

2.1. Chemicals

Phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol were purchased from Aldrich in the quality of chromatography standards. Methanol, ethanol and water were of analytical grades and were received from Fluka. NaOH, HCl came from Penta and phthalocyanines used – ZnPHC, SiPHC, AlPHC, metal-free PHC (MefreePHC), were prepared and chemically modified in our laboratories as already described [23].

2.2. Photocatalytic experiments

These tests were carried out in a magnetically stirred batch reactor (reaction volume 200 ml, saturated with air) illuminated either with photons in the visible region (three fluorescent tubes Narva Yellow Special 016, emission interval 500–700 nm, maximum at 580 nm, verified on spectrofluorometer Fluoromax 2, Jobin Yvon, nominal output 18 W, irradiation intensity 100 mm 1.52 mW/cm² – Si photodiode Hamamatsu S1337-BQ), or with photons in the UV region (three Narva Blacklight Blue 073 lamps, emission interval 330–400 nm, verified on spectrofluorometer Fluoromax 2, Jobin Yvon, nominal output 18 W each, irradiation intensity 2.65 mW/cm² – UV Light Meters, Mannix Interstate). Phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol were dissolved in HPLC grade water (1 × 10^{−4} mol l^{−1}). The water solution of each PHC in the form of the sodium salt of its sulphoacid was introduced as a catalyst (7 × 10^{−6} mol l^{−1}). In all experiments a constant pH was established and maintained (NaOH solution) by means of the automatic titration equipment Titrator Manager TIM 856 (TitraLab) with a combined pH electrode (radiometer).

2.3. Analytical

Samples of reaction mixtures were analysed by HPLC (Shimadzu LC 20A Prominence) with MERCK LiChroCART 125-4 column or LiChroCART 250-4 with Lichrospher RP-18 Stationary phase. Methanol/water mobile phase was 40/60. Detection wavelengths were selected at the maximum

absorption for each substrate (phenol 288 nm, 2-chlorophenol 294 nm, 3-chlorophenol 292 nm, 4-chlorophenol 298 nm, 2,6-dichlorophenol 300 nm, 2,4,6-trichlorophenol 305 nm). Spectral characterisation (positions of absorption bands and qualitative assessment of the presence of dimeric PHC forms) was carried out on a UV–vis spectrophotometer (Cary 100 UV–vis, Varian).

2.4. Quantum yields

Values of quantum yields ϕ were evaluated according to Eq. (1).

$$\Phi = \frac{k \times V \times c_i}{J_{hv} \times A} \times 100 \quad (1)$$

where J_{hv} is the incident photon flux intensity (Einstein s^{−1} m^{−2}, Eq. (2)), V represents the reaction volume (m³), c_i is the initial concentration of the substrate (mol m^{−3}), A is the illuminated area (m²) and k is the rate constant (s^{−1}). For determination of rate constants k first order kinetics was assumed for all reactions.

$$J_{hv} = \frac{\lambda \times P_f}{h \times \gamma \times N_A} \quad (2)$$

where P_f is the experimentally measured irradiation intensity (W m^{−2}), λ is the maximum wavelength of the used illumination source, h is the Planck constant 6.626 × 10^{−34} J s, γ is the light velocity in vacuum (3 × 10⁸ m s^{−1}) and N_A is the Avogadro number (6.022 × 10²³ mol^{−1}).

3. Results and discussion

It must be emphasised that the constituent phthalocyanine skeleton is virtually insoluble either in polar or non-polar solvents. All PHCs used in this work, thus, had to be chemically modified first [23] by introducing a specific functional group (–SO₃H) to the benzene rings of the PHC skeleton to improve their solubility in water. On the other hand, these soluble modifications tend to aggregate [24–26] to form dimeric structures known for their limited photoactivity as described, e.g. at [27–29].

Experiments using a monochromatic source of light capable of well distinguishable and strictly separate illumination of the monomeric and dimeric forms could provide quantification of this phenomenon. Such experiments are now in progress and will be subjects of our next communication. Another possibility to avoid the problem of dimerisation could be based on heterogenisation of phthalocyanines by distributing them in a zeolite supercage. In this case the problem of solubility is not counted anymore, because they behave as standard heterogeneous catalysts [30–32].

The region of the photon flux absorption in the visible region is relatively wide for all the tested phthalocyanines. It is usually referred to as the Q-band and is responsible for the characteristic blue colour of these molecules. These strong absorptions span approximately from 550 to 700 nm (Fig. 1)

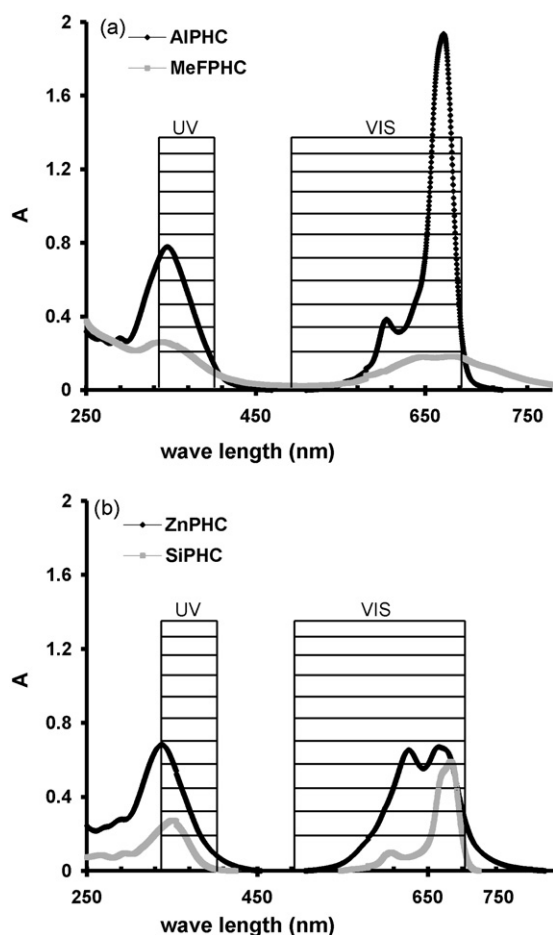


Fig. 1. (a) Absorption spectra of sulphonated AIPHC and metal-free PHC in water with the area illuminated in photocatalytic reactions, $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$. (b) Absorption spectra of sulphonated ZnPHC and SiPHC in water with the area illuminated in photocatalytic reactions, $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$.

covering both the monomeric and dimeric forms. The less intensive bands located at lower wavelengths correspond to the dimers. However, as typically for AIPHC and SiPHC, the dimeric forms are much less pronounced. Presence of any aggregates could not be extracted from the absorption behaviour in the UV region, where only a single broad absorption band appears. The prevalent monomer behaviour of Si and Al phthalocyanines bears on the existence of axial ligands [33] on the central metal atom in the axial direction to the molecular plane. There are two characteristic axial OH ligands in SiPHC forming an octahedral structure and one OH ligand in AIPHC giving a tetrahedral pyramid structure for the phthalocyanine molecule (Fig. 2a and b). On the other hand, ZnPHC and metal-free phthalocyanines are virtually planar molecules (Fig. 2c and d) with no axial ligands and thus with higher tendency for aggregation.

In our recent paper [23] we described the preparation of a large series of phthalocyanines, optimisation of experimental conditions and their photocatalytic performance in a model decomposition reaction. Here we are focused on the description of the photocatalytic properties of four phthalocyanines (AIPHC, SiPHC, ZnPHC, MefreePHC) in oxidative decompositions of phenol and a series of its chlorinated derivatives 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-CP) and 2,4,6-trichlorophenol (2,4,6-CP). Lamp intensities in both regions were low enough and no decomposition of these compounds occurred without phthalocyanines. The original reaction mechanism [34] was assumed and it was based on the analytically proven concept of the simple reaction intermediates and products (quinone, hydroquinone, maleic acid, fumaric acid, hydrochloric acid, etc.). Previously, only the relative decrease of the initial reactant concentration was evaluated. Raw experimental results were plotted as a dependence of the natural logarithm of the relative concentration of the substrate versus time. Kinetic parameter – quantum yields are listed in Tables 1 and 2.

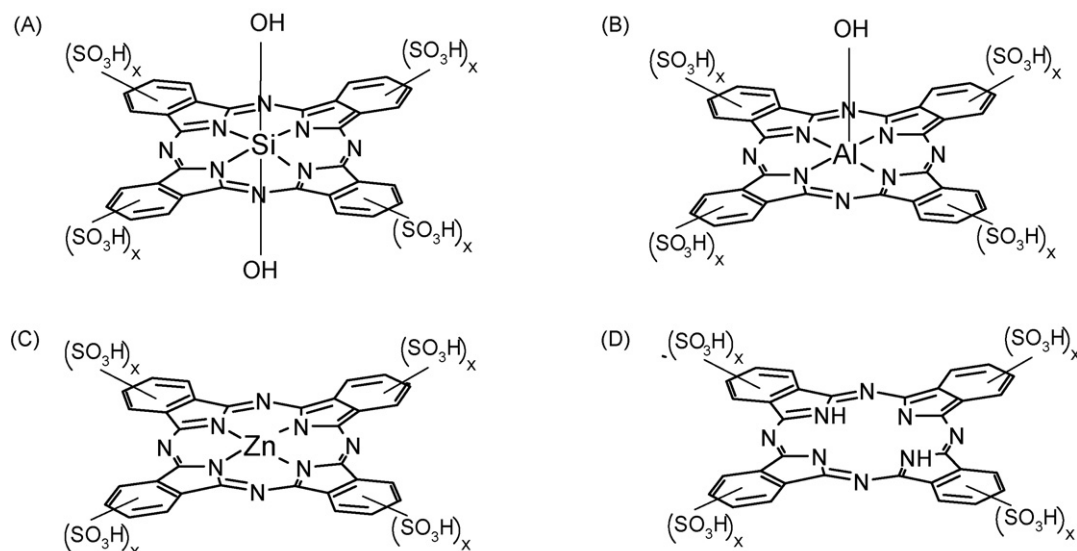


Fig. 2. Structure of sulphonated derivatives of SiPHC (A), AIPHC (B), ZnPHC (C) and metal-free PHC (D).

Table 1
Quantum yields for reactions with sulphonated AIPHC at various pH

pH	Φ (%)					
	Phenol	2-CP	3-CP	4-CP	2,6-CP	2,4,6-CP
10	0.39	0.43	0.48	0.61	0.47	0.40
9	0.11	0.39	0.27	0.16	0.36	0.29
8	0.03	0.15	0.11	0.16	0.30	0.25

Table 2
Quantum yields for reactions with sulphonated AIPHC, ZnPHC and SiPHC at pH 10

	Φ (%)					
	Phenol	2-CP	3-CP	4-CP	2,6-CP	2,4,6-CP
AIPHC	0.39	0.43	0.48	0.61	0.47	0.40
SiPHC	0.24	0.31	0.27	0.44	0.31	0.25
ZnPHC	0.15	0.24	0.20	0.20	0.21	0.20

Initially the effect of pH was assessed and this parameter was carefully optimised for all reactants with AIPHC. In experiments with phenol and its chlorinated derivatives, activities evaluated at various values of pH differed significantly (Fig. 3a and b). The optimum level was found at pH \sim 10. On the other hand, the influence of this parameter for the di- and tri-chlorinated derivatives was much less pronounced. These results are in compliance with the magnitudes of their pK_a values (dissociation constants). Phenol and monochlorophenols reveal pK_a values in the range of 9–10, which means that at pH 9–10 an equilibrium between the dissociated (phenolates) and non-dissociated (phenols) forms is established. Phenolates undergo oxidation incomparably more easily than their non-dissociated forms, thus higher alkalinity of the solution is an essential factor influencing the reaction rate. Dissociation constants pK_a of di- and tri-chlorophenols are lower (\sim 7) and thus the effect of pH is less significant. Quantum yields in Table 1 for AIPHC evidently reflect this phenomenon.

All chlorinated derivatives were transformed at higher rates than phenol and 4-CP was identified as the most reactive molecule and that with the highest achieved quantum yield of 0.61% at pH 10 (Table 2). Among the monochlorinated derivatives, 4-CP is the symmetrical one and due to steric effects its reactivity is higher. Relatively low stabilities of 2,6-CP and 2,4,6-CP upon contact with singlet oxygen was not expected, however, from a practical point of view it represents an important finding. It must be emphasised that quantum yields of these homogeneous reactions are at least comparable with those typically reported [35] for systems using particulate TiO_2 as the photocatalyst. All three PHCs could be referred to as active (at pH 10). This is in agreement with the anticipated concept of the singlet oxygen generation only by PHCs with a specific electronic molecular structure. The excited triplet states with longer lifetime are characteristic for porphyrins involving metal ions with completely occupied valence sphere or d-orbitals (e.g. AIPHC, SiPHC, ZnPHC). Experiments quantifying the number of these photo-generated active species are now in progress and the results will be reported soon.

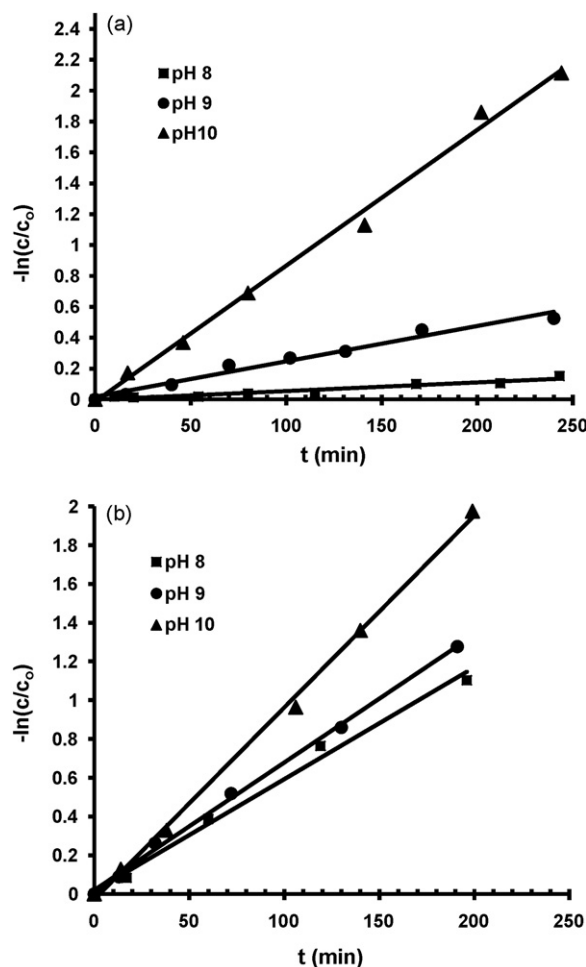


Fig. 3. Photooxidation of phenol (a) and 2,4,6-trichlorophenol (b) catalysed with sulphonated AIPHC in the visible light region ($c_{4-CP(\text{initial})} = 1 \times 10^{-4}$ mol/dm³, pH 10).

Despite the generally good activities of these three PHCs, photoactivity of AIPHC was always distinctively higher for all tested reactants. Finally, it should be added that under standard experimental conditions MefreePHC was virtually inactive as discussed later.

As already mentioned, some soluble sulphonated phthalocyanines tend to aggregate. Dimerisation might be simply suppressed by addition of another co-solvent, typically of alcohol (here ethanol). Absorption spectra are shown (Fig. 4a and b) for ZnPHC and MefreePHC dissolved in a series of various water–alcohol mixtures. When dissolving ZnFTC in ethanol instead of water, the solution's originally bimodal spectrum with two nearly identical bands changes to the spectrum of the monomeric form with only one dominating band. Already at the molar ratio water-to-alcohol = 1, the absorption band characteristic for the dimer is insignificant. The originally very diffuse band, due to the strong contribution of both monomer and dimer forms for MefreePHC in water, changes significantly upon addition of alcohol as the co-solvent. The dimer band becomes recognizable because of the intensive sharpening of the second band corresponding with the monomer form. The trend is similar as previously, however,

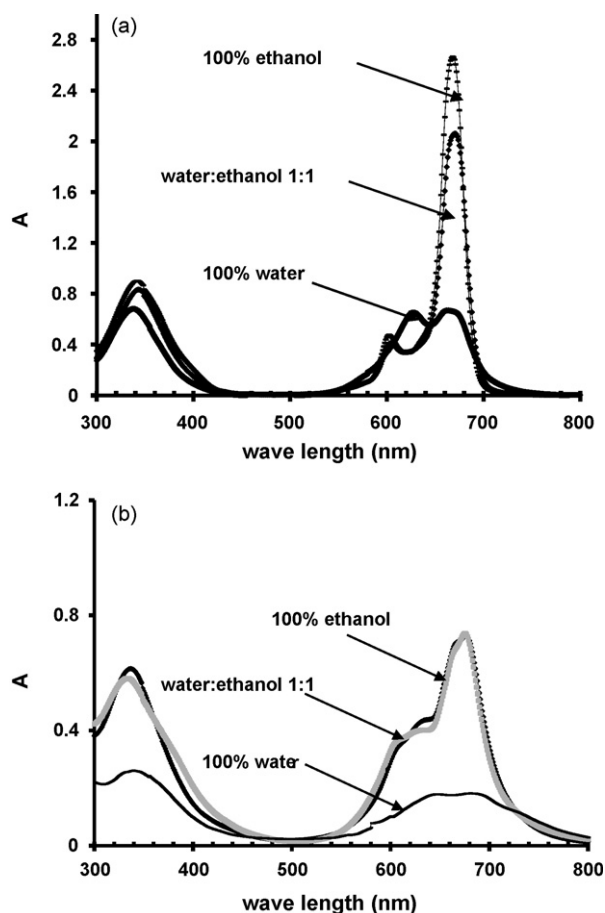


Fig. 4. Absorption spectra of sulphonated ZnPHC (a) and metal-free PHC (b) ($c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$) with the variable amount of alcohol added to the water environment.

the spectra measured for pure alcohol and the 1:1 mixture are already identical. It must be noted that the effect of the co-solvent addition is virtually zero in case of PHCs with lower aggregation tendencies (AIPHC, SiPHC).

Suppression of the presence of the dimeric form should be reflected in the enhanced activities of these two PHCs (ZnPHC, MefreePHC) and was verified in the decomposition of 4-CP. The positive effect of the alcohol co-solvent is especially apparent for MefreePHC. Despite that the absorption spectra of this phthalocyanine in pure ethanol and in the mixture of water and ethanol 1:1 (Fig. 5a) are nearly identical, the reaction does not proceed in pure alcohol. The same phenomenon could be observed also for ZnPHC. Its reaction rate in alcohol is almost zero in spite of the prevailing existence of the monomer form and the optimum molar ratio water:alcohol again being 1:1 (Fig. 5b). It is important to note that activities of the two highly active PHCs (AIPHC, SiPHC) are also significantly reduced if water is completely exchanged with ethanol as the reaction solvent.

As already discussed, there is also a strong absorption of a typical PHC molecule in the UV region spanning from 300 to 400 nm. Kinetic parameters for oxidation of 4-CP were already discussed in our recent paper [23]. It was shown that the parameter of quantum yield Φ , reflecting the quantitative

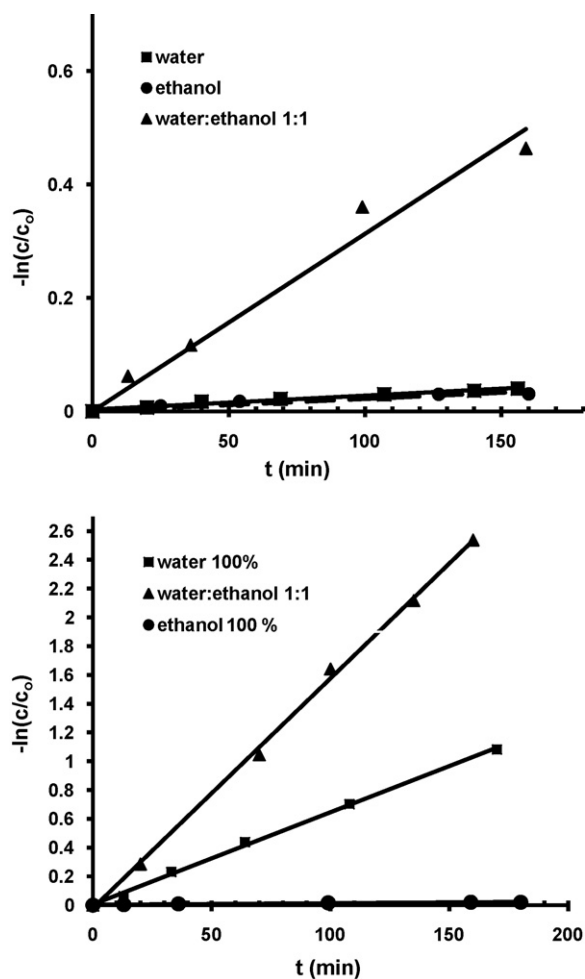


Fig. 5. Photooxidation of 4-CP catalysed by sulphonated metal-free PHC (a) and ZnPHC (b) with different amounts of water and ethanol ($c_{4\text{-CP}(\text{initial})} = 1 \times 10^{-4} \text{ mol/dm}^3$, $c_{\text{PHC}} = 7 \times 10^{-6} \text{ mol/dm}^3$, pH 10)—visible light region.

relationship between the number of reacting molecules and the total number of involved photons, was higher for reactions carried out with UV. The same fact was validated in this study for other tested chlorophenols and it might be generalised. The trends for other members of the tested group of chemicals (phenol, 2-CP, 3-CP, 4-CP, 2,4-CP, 2,4,6-CP) were analogous to those observed for these compounds in the visible region (good reactivity of chlorinated phenols, steric effects, activities of PHCs, role of pH). As calculated, the light source in the visible region emits more photons than that emitting in UV. In the UV region photons are more abundant in energy, however, the essential parameter is represented by the number of photons rather than their energies (anticipated stoichiometry is: one incident photon = one transformed molecule).

In other words, unlike our observations, reactions in the visible region should be favoured. Interpretation of this contradiction might be sought in terms of the exact positions of UV and visible emission lamp spectra. The emission spectrum of the UV source covered perfectly the very strong absorbance band of the three studied phthalocyanines and it

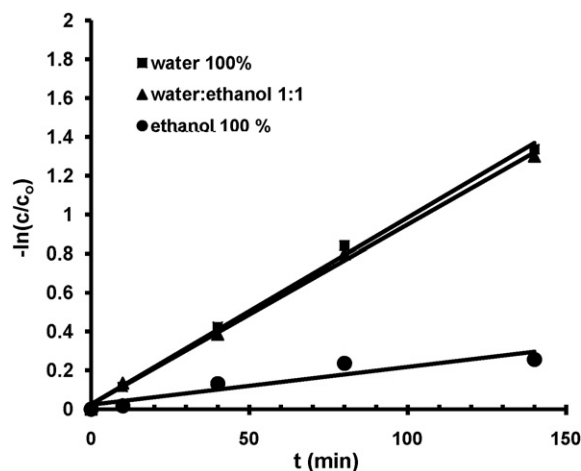


Fig. 6. Photooxidation of 4-CP catalysed by sulphonated ZnPHC with different amount of water and ethanol ($c_{4\text{-CP}}(\text{initial}) = 1 \times 10^{-4} \text{ mol/dm}^3$, $c_{\text{PHC}} = 7 \times 10^{-6} \text{ mol/dm}^3$, pH 10)—UV light region.

might be expected that most of the incident photons were effectively absorbed. On the other hand, the maximum in the emission spectrum of the visible light source was shifted slightly towards the yellow colour compared with the maximum of the PHCs' absorption and it might be expected that only a certain proportion of incident photons were effectively absorbed. This point will be clarified in the currently running experiments using an optical bench, sophisticated focusing geometry and a system of precise filters.

Finally, it was proven that under UV illumination the positive role of the co-solvent (ethanol) was not so significant and that reactions proceeded at similar rates both in pure water and in the mixture of water and ethanol (1:1) as shown in Fig. 6 for 4-CP and ZnPHC. The total stop-effect of pure alcohol was, however, observed.

4. Conclusions

Members of a series of chemicals involving phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol were oxidised with the help of four modified synthetic porphyrins—phthalocyanines AlPHC, SiPHC, ZnPHC and MefreePHC. The knowledge of their behaviour upon photon flux absorption (both UV and visible) is essential for understanding to their catalytic performance in these reactions. This and the previous work [23] summarise initial experiments focused on the overall assessment of the photocatalytic activity of the produced and modified phthalocyanines and on the introductory discussion of the most important factors influencing these reactions. The advanced research based on the quantification of the photo-generated singlet oxygen species and on evaluation of parameters affecting the extent of this generation is currently in progress and the results will be reported soon.

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References

- [1] G. Angeletti, A. Björseth, *Organic Micropollutants in Aquatic Environment*, Kluwer Academic Publishers, Dordrecht, 1991.
- [2] L. Vlkova, V. Cirkva, *Chem. Listy* 99 (2005) 125.
- [3] J.A. Bumpus, M. Tien, D. Wright, S. Aust, *Science* 228 (1985) 1434.
- [4] S. Fetzner, F. Lingnes, *Microbiol. Rev.* 58 (1994) 641.
- [5] N. Pal, G. Lewandowski, P.M. Armenante, *Biotechnol. Bioeng.* 46 (1995) 599.
- [6] V. Janda, M. Svecova, *Chem. Listy* 94 (2000) 905.
- [7] B. Meunier, A. Sorokin, *Acc. Chem. Res.* 30 (1997) 470.
- [8] A. Sorokin, S. De Suzzoni-Dezard, D. Poullain, J.-P. Noel, B. Meunier, *J. Am. Chem. Soc.* 118 (1996) 7410.
- [9] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [10] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735.
- [11] B. Meunier, *Chem. Rev.* 92 (1992) 1411.
- [12] V. Augugliario, L. Palmisano, M. Chiavella, A. Sclafani, L. Marchese, G. Martra, F. Miano, *Appl. Catal.* 69 (1991) 323.
- [13] J.C. Yu, Y. Xie, H.Y. Tang, L. Zhang, H.C. Chan, J. Zhao, *J. Photochem. Photobiol. A* 156 (2003) 235.
- [14] V. Iliev, *J. Photochem. Photobiol. A* 151 (2002) 195.
- [15] J. Moon, C.Y. Yun, K.-W. Chung, M.-S. Kang, J. Yi, *Catal. Today* 87 (2003) 77.
- [16] V. Iliev, D. Tomova, L. Bilzarska, L. Prahov, L. Petrov, *J. Photochem. Photobiol. A* 159 (2003) 281.
- [17] K. Lang, J. Mosinger, D. Wagnerova, *Chem. Listy* 99 (2005) 211.
- [18] K. Ozoemena, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A* 139 (2001) 217.
- [19] K. Ozoemena, N. Kuznetsova, T. Nyokong, *J. Mol. Catal. A* 179 (2001) 29.
- [20] R. Gerdes, D. Wohrle, W. Spiller, G. Schneider, G. Schnurpfeil, G. Schultz-Ekloff, *J. Photochem. Photobiol. A* 111 (1997) 65.
- [21] B. Agboola, K. Ozoemena, T. Nyokong, *J. Mol. Catal. A* 248 (2006) 84.
- [22] A.K. Sobbi, D. Woehre, D. Schlettwein, *J. Chem. Soc., Perkin Trans. 2* (1993) 481.
- [23] P. Kluson, M. Drobek, T. Strasak, J. Krysa, M. Karaskova, J. Rakusan, *J. Mol. Catal. A* 272 (2007) 213.
- [24] J. Edrei, V. Gottfried, J.E. van Lier, S. Kimel, J. Porphyrins Phthalocyanines 2 (1998) 191.
- [25] P.C. Martin, M. Gouterman, B.V. Pepich, G.E. Renzoni, D.C. Schindele, *Inorg. Chem.* 30 (1991) 3305.
- [26] D. Dhami, D. Philips, *J. Photochem. Photobiol. A* 100 (1996) 77.
- [27] W. Spiller, D. Woehrle, G. Schulz-Ekloff, W.T. Ford, G. Schneider, J. Stark, *J. Photochem. Photobiol. A* 95 (1996) 161.
- [28] V. Iliev, A. Ileva, *J. Mol. Catal. A* 103 (1995) 147.
- [29] V. Iliev, V. Alexiev, L. Bilyarska, *J. Mol. Catal. A* 137 (1999) 15.
- [30] A. Zsigmond, F. Notheisz, M. Bartok, J.E. Backvall, *Stud. Surf. Sci. Catal.* 78 (1993) 417.
- [31] A. Zsigmond, F. Notheisz, J.E. Backvall, *Catal. Lett.* 65 (2000) 135.
- [32] R. Raja, P. Ratnasamy, *Appl. Catal. A* 143 (1996) 145.
- [33] J.R. Mooney, C.K. Choy, K. Knox, M. Kenney, *J. Am. Chem. Soc.* 97 (1975) 3033.
- [34] V. Iliev, A. Mihaylova, L. Bilyarska, *J. Mol. Catal. A* 184 (2002) 121.
- [35] H. Krysova, J. Krysa, K. Macounova, J. Jirkovsky, *J. Chem. Technol. Biotechnol.* 72 (1998) 169.